EDGEWOOD CHEMICAL BIOLOGICAL CENTER
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
Aberdeen Proving Ground, MD 21010-5424

ECBC-TR-1373

CHEMICAL ATTRIBUTION SIGNATURES OF CYANOGEN CHLORIDE FROM COMMERCIAL SOURCES

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RESEARCH AND TECHNOLOGY DIRECTORATE

October 2016

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REPORT DOCUMENTATION PAGE			*Form Approved* *OMB No. 0704-0188*
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1. REPORT DATE *(DD-MM-YYYY)* XX-10-2016	**2. REPORT TYPE** Final		**3. DATES COVERED** *(From - To)* Sep 2012 – Aug 2013
4. TITLE AND SUBTITLE Chemical Attribution Signatures of Cyanogen Chloride from Commercial Sources			**5A. CONTRACT NUMBER** **5b. GRANT NUMBER** **5c. PROGRAM ELEMENT NUMBER**
6. AUTHOR(S) Cullinan, David B.			**5d. PROJECT NUMBER** 02P-0199 **5e. TASK NUMBER** **5f. WORK UNIT NUMBER**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Director, ECBC, ATTN: RDCB-DRC-F, APG, MD 21010-5424			**8. PERFORMING ORGANIZATION REPORT NUMBER** ECBC-TR-1373
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of Homeland Security, Science and Technology Directorate, 245 Murray Lane, SW, Mail Stop 2100, Washington, DC 20528-2100			**10. SPONSOR/MONITOR'S ACRONYM(S)** DHS-ST **11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT: Department of Homeland Security's Science and Technology Directorate has expressed an interest in the discovery of chemical attribution signatures (CAS), which are used to provide a link between a given hazardous chemical and its source (i.e., a synthetic pathway or a commercial vendor). CAS are generally impurities present in a final product that are indicative of its source. Since 2005, the U.S. Army Edgewood Chemical Biological Center Forensic Analytical Center members have performed purity analyses on >70 cylinders of cyanogen chloride (CK) procured from three different commercial vendors. This study provides CAS data that are relevant to the three vendors and also examines production differences in CK over time.			
15. SUBJECT TERMS Cyanogen chloride (CK) — Gas chromatography–thermal conductivity detector (GC/TCD) Hydrogen cyanide (AC) — Magnetic resonance spectroscopy Commercial source — Carbon tetrachloride (CCl_4) Attribution signature			

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Renu B. Rastogi
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U	UU	30	(410) 436-7545

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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PREFACE

The work described in this report was authorized under project number 02P-0199 and Interagency Agreement number HSHQPM-12-X-00173 as part of the Department of Homeland Security Chemical Forensics Program. The work was started in September 2012 and completed in August 2013.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgments

The authors acknowledge the following individuals for their hard work and assistance with the execution of this technical program:

- Jadey Pareja and Juanita Villanueva (U.S. Army Edgewood Chemical Biological Center [ECBC] Protective Equipment Team), for their assistance in matching cyanogen chloride (CK) cylinder orders with the manufacturers; and

- Timothy Allan, Alex Jestel, and other members of the ECBC Forensic Analytical Center for their expertise in CK analysis by gas chromatography–thermal conductivity detection.

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CHEMICAL ATTRIBUTION SIGNATURES OF CYANOGEN CHLORIDE FROM COMMERICAL SOURCES

1. INTRODUCTION

Since 2005, members of the U.S. Army Edgewood Chemical Biological Center (ECBC) Forensic Analytical Center (FAC), which is an International Organization for Standardization 17025-certified analytical laboratory, have collaborated with the ECBC Protective Equipment Team (PET) to perform purity analyses on samples from cylinders containing phosgene (CG), cyanogen chloride (CK), and hydrogen cyanide (AC). The majority of that work has been focused on CK. The PET members require certified documentation of the purity of these chemical agents for the tests they perform for their customers. During this collaboration, FAC members have analyzed over 70 CK cylinders, as well as several AC and CG cylinders, for purity. The primary analytical methods used have been gas chromatography–thermal conductivity detection (GC/TCD) and nuclear magnetic resonance (NMR) spectroscopy. In these analyses, the contaminating species have been identified wherever possible, with successful identification more common in the more recent analyses.

There are relatively few commercial sources for these gases. Since 2005, PET members have procured CK from the same three vendors, although these vendors' company names have changed over time. PET members have maintained records for the purchase of each cylinder, and this information has been cross-referenced with the data of agent analyses kept by the FAC team. The purchase records from between 2005 and 2013 and original data of agent analyses were re-examined for this study for the following purposes:

- to identify potential chemical attribution signatures (CAS) for CK,
- to determine whether any of these CAS are specific to a particular vendor, and
- to examine whether the CAS have changed for these vendors over the time frame of these analyses.

2. METHODS

No new analyses were performed for this study, which focused on re-examination and data mining of purity analysis reports from 2005 through 2013. The primary analytical methods used for these analyses were GC/TCD and carbon 13 (^{13}C)-NMR spectroscopy.

2.1 Gas Chromatography–Thermal Conductivity Detection

The GC/TCD method used by the ECBC FAC team for CK analysis included a sample loop connected to the cylinder to allow sampling of the neat gas. Retention times for the impurities found in these cylinders were verified by comparison with authentic standard materials, and most were confirmed by GC mass spectrometry. Samples were analyzed in triplicate on an Agilent (Agilent Technologies, Inc., Santa Clara, CA) GC system (the model changed over the time frame of these studies) using a DB-624 column, with air blanks used between samples.

Before the analysis was started, a CK cylinder was purged for at least 1 h with the valve opened to approximately 1–3 psi. Each CK cylinder was known to have a "plug" of CO_2 as a result of the filling process. If a cylinder had been analyzed without purging, the CO_2 would have accounted for as much as 30% of the total area of the chromatogram. In addition, based on the GC and detector systems used, it was necessary to determine the appropriate sample injection volume that would not saturate the CK peak response but would allow for the detection of impurity peaks of approximately 0.05% of the total area under the chromatographic curve. A typical GC chromatogram of CK is shown in Figure 1.

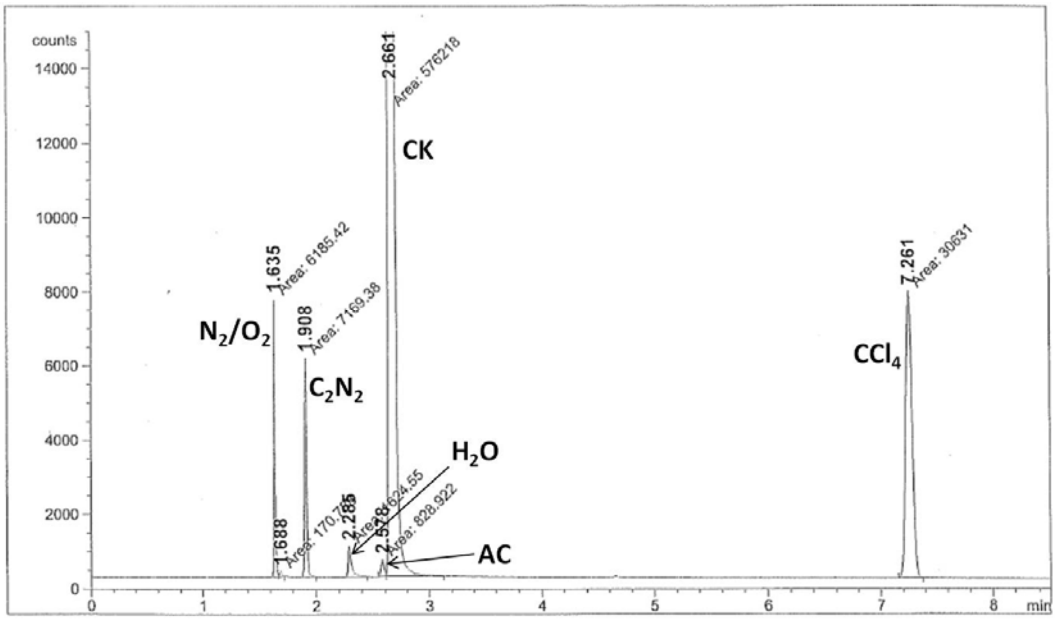

Figure 1. A typical GC chromatogram, expanded to show impurities.

2.2 Nuclear Magnetic Resonance Spectroscopy

Purity analysis by NMR spectroscopy was carried out as described by Henderson and Cullinan.* The samples were prepared in pressure- and vacuum-valve NMR tubes (Wilmad Labglass [Vineland, NJ], which were 528-PV-9 or equivalent) by immersing the stem of the NMR tube in a dry ice and acetone bath and condensing a stream of the gas from the cylinder into the tube. It was important to condense the gas using something colder than a standard ice bath because some common impurities (e.g., cyanogen [C_2N_2]) have boiling points well below 0 °C. NMR spectroscopy was carried out at a sample temperature of 10 °C (i.e., below the CK boiling point).

* Henderson, T.J.; Cullinan, D.B. Purity Analysis of Hydrogen Cyanide, Cyanogen Chloride and Phosgene by Quantitative ^{13}C NMR Spectroscopy. *Magn. Reson. Chem.* **2007**, *45*, 954–961.

This work was carried out on a Bruker (Bruker Corporation, Billerica, MA) NMR spectrometer (primarily an Avance DRX or Avance III 300 MHz system, although work was also carried out using an Avance DRX 500 MHz system). The primary NMR investigation performed was a ^{13}C-NMR experiment with inverse-gated ^{1}H decoupling using a relaxation delay greater than 8 × T_1 to ensure quantitative response. A typical ^{13}C-NMR spectrum of CK is shown in Figure 2. Although no ^{1}H signals were expected from a neat CK sample, ^{1}H-NMR spectroscopy was carried out, in the interests of identifying additional impurities. However, because CK provided no ^{1}H signals, any impurities detected only in the ^{1}H spectrum could not be quantitatively included in the purity determination.

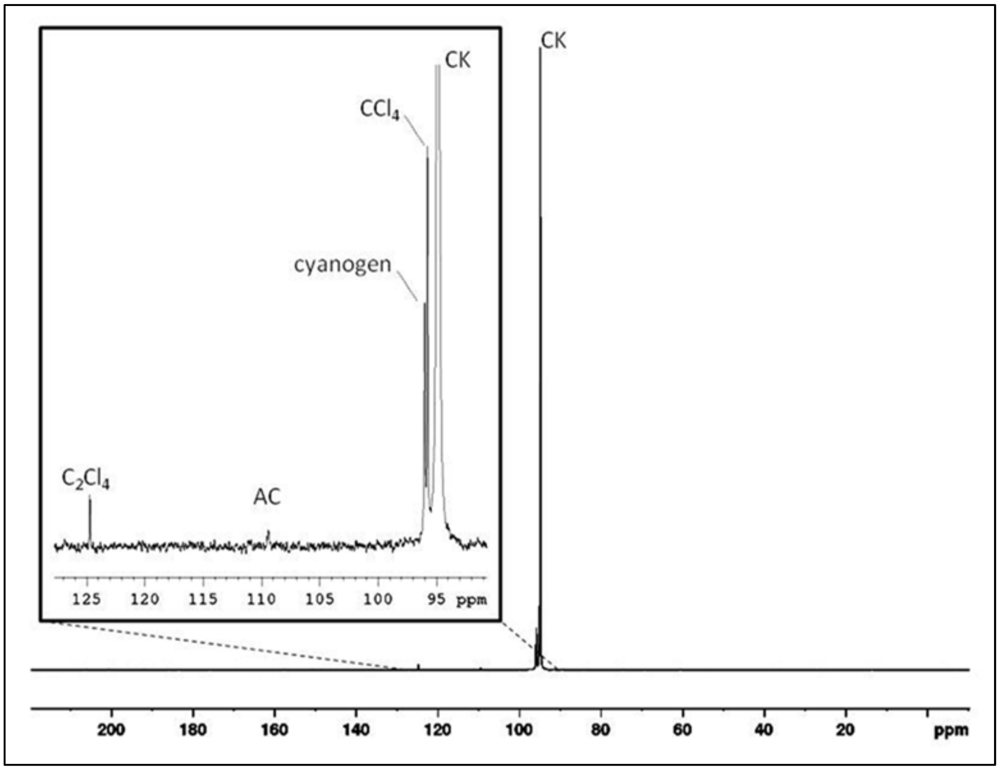

Figure 2. ^{13}C-NMR spectrum of CK. Inset shows an expanded view in which impurities are labeled.

3. RESULTS AND DISCUSSION

3.1 Purity Analysis

Purity analyses from 74 CK cylinders were examined in this data mining effort. These CK cylinders included 6 procured in 2005, 1 procured in 2006, 4 procured in 2008, 10 procured in 2009, 23 procured in 2010, 13 procured in 2011, 12 procured in 2012, and 5 procured in 2013. Of these, one cylinder was discarded because its vendor could not be verified. Another cylinder, purchased from Custom Gas Solutions (Durham, NC), was discarded as an anomaly because it contained over 20% CO_2, even after the purging process. The remaining 72 cylinders included 28 from HP Gas, LLC (Baytown, TX), including Stillwater Consultants (Stillwater, MN), LMTG (Roanoke, LA), and TL2 Gases (Sulphur, LA); 28 from

Semiconductor Resources including Specialty Gases of America (Toledo, OH); and 16 from Custom Gas Solutions.

The three impurities commonly seen in the ^{13}C-NMR spectrum were C_2N_2, carbon tetrachloride (CCl_4), and ethylene tetrachloride (C_2Cl_4). AC was only detected by ^{13}C-NMR spectroscopy at one time at levels that were strong enough to quantify. In two other cylinders, AC was seen in the ^{13}C-NMR spectrum, but it was not a strong enough signal to be reliably integrated. In the GC chromatogram, the impurities commonly identified were nitrogen and oxygen (i.e., common air components that could not be separated by the GC technique), carbon dioxide (CO_2), water (H_2O), C_2N_2, CCl_4, and AC.

Complete listings of the impurities detected in the CK purity analyses by each technique, as well as the percent concentration of each, are listed in the appendixes of this report. Appendix A lists the data analyses in reverse chronological order of when they were initially analyzed. In Appendixes B–D, that list is broken down by vendor; the data analyses are listed in reverse chronological order within each vendor group.

3.2 Attribution Signatures

Three trends were noticed in the data analyses, which may indicate patterns usable for attribution purposes (i.e., each of these were trends and not clear indicators):

- CCl_4 detection,
- CCl_4 concentration, and
- H_2O and AC by ^1H NMR

3.2.1 Carbon Tetrachloride Identification by Gas Chromatography–Thermal Conductivity Detection

Analysis by GC/TCD showed that 22 of the 28 CK cylinders from HP Gas and 15 of the 16 cylinders from Custom Gas Solutions contained detectable levels of CCl_4. On the other hand, only 3 of the 28 CK cylinders from Semiconductor Resources showed a quantifiable signal for CCl_4 in the chromatogram.

This GC/TCD data provides an example of how the trends of these attribution signatures can be used. In these data sets, CCl_4 was detected in about 78% of the CK cylinders from HP Gas, about 93% of the cylinders from Custom Gas Solutions, and only about 10% of the cylinders from Semiconductor Resources. Analysis of any single cylinder found to lack CCl_4 would not unambiguously prove that it was procured from Semiconductor Resources; however, it would indicate that Semiconductor Resources was a likely source. Analyses of several cylinders that all showed the same trend would greatly increase the accuracy of that determination.

This trend was less defined by NMR, most likely because the CCl_4 peak in the NMR spectrum was on the downfield slope of the much larger and stronger CK peak; therefore, the CCl_4 peak was easily obscured by the CK peak.

3.2.2 Carbon Tetrachloride Concentration by Gas Chromatography–Thermal Conductivity Detection

While a lack of CCl_4 identified in the GC/TCD chromatogram indicated Semiconductor Resources as a likely vendor source, a relatively high concentration of CCl_4 provided additional information. An examination of the CCl_4 concentrations in CK samples from HP Gas shows that, in the 15 analyses from 2011 through 2013, the highest concentration of CCl_4 detected by GC/TCD was 0.6%. Of the 13 analyses done between 2005 and 2010, all but two showed concentrations of 0.9% or more, with an average of 3.8%.

Of the 15 CK cylinders from Custom Gas Solutions that were analyzed in which CCl_4 was detected (3 from 2009, 8 from 2010, and 4 from 2012), only 2 showed concentration levels higher than 1%. Not surprisingly, given that CCl_4 was detected in only 3 of the 28 cylinders from Semiconductor Resources, none of these cylinders showed CCl_4 concentration levels above 1%.

This suggests that a cylinder from an unknown commercial source that shows more than a 1% concentration level of CCl_4 may be an older cylinder from HP Gas. Therefore, this trend could represent a possible attribution signature, not only for a specific vendor but also to a time of production.

3.2.3 Water and Hydrogen Cyanide Identification by ^{1}H-NMR Spectroscopy

As mentioned in Section 2.2, ^{1}H-NMR spectra were collected for the majority of the CK analyses done by NMR, in the interest of recognizing additional impurities. CK contains no hydrogen; therefore, a sample of pure CK should reveal nothing in the ^{1}H-NMR spectrum. In addition, the common impurities (i.e., C_2N_2, CCl_4, and C_2Cl_4) that were observed during the analyses have no hydrogen. ^{1}H-NMR is able to detect compounds in the parts-per-million range, so impurities that were well under 0.1% levels in these samples could easily have been detected if they had contained hydrogen.

In most of the ^{1}H-NMR spectra, the strongest resonance detected came from H_2O, as confirmed by a simple spiking experiment. In all of the samples of CK cylinders from HP Gas for which ^{1}H-NMR spectra were collected, there were two strong and clear signals in the ^{1}H spectrum: H_2O and AC (this was also confirmed through spiking). If AC had been present in the sample at a concentration greater than about 0.1%, it would have been quantified in the ^{13}C-NMR spectrum. Therefore, despite the clarity of the signals in the ^{1}H-NMR spectra, the actual concentrations were likely lower. Nonetheless, the presence of H_2O and AC as clear resonances in the ^{1}H-NMR spectrum was very consistent in the HP Gas samples.

Similar ^{1}H-NMR spectra were seen in only a few of the samples from each of the other two vendors, including two in which AC gave a stronger resonance signal than H_2O. A similar pattern in the CK ^{1}H-NMR spectra to that of CK from HP Gas was observed in 3 of the 11 cylinders from Custom Gas Solutions and 2 of the 19 cylinders from Semiconductor Resources. (It should be noted that the only sample for which AC was strong enough to be quantified in the ^{13}C-NMR spectrum came from Semiconductor Resources.) For the majority of the spectra from the other vendors, however, the H_2O signal was quite weak or broad, and the AC signal was often not seen at all.

Given the qualitative nature of the results from the ^{1}H-NMR spectra, a compilation of the ^{1}H-NMR spectra from samples from the different vendors is included in Figure 3. The top panel of that figure shows ^{1}H-NMR spectra of samples from HP Gas, and the following two panels show spectra of samples from Semiconductor Resources and Custom Gas Solutions. Each panel shows ^{1}H-NMR spectra offset from each other vertically and horizontally, for ease of viewing. In each panel, the spectra have been normalized relative to the intensity of the H_2O signal (2.17 ppm) and displayed in reverse chronological order from front to back. Note that the baselines in some of the spectra in the bottom two panels appear noisy, indicating that the H_2O resonance signals were very low, to such an extent that by normalizing the signal from H_2O, the baseline was over expanded.

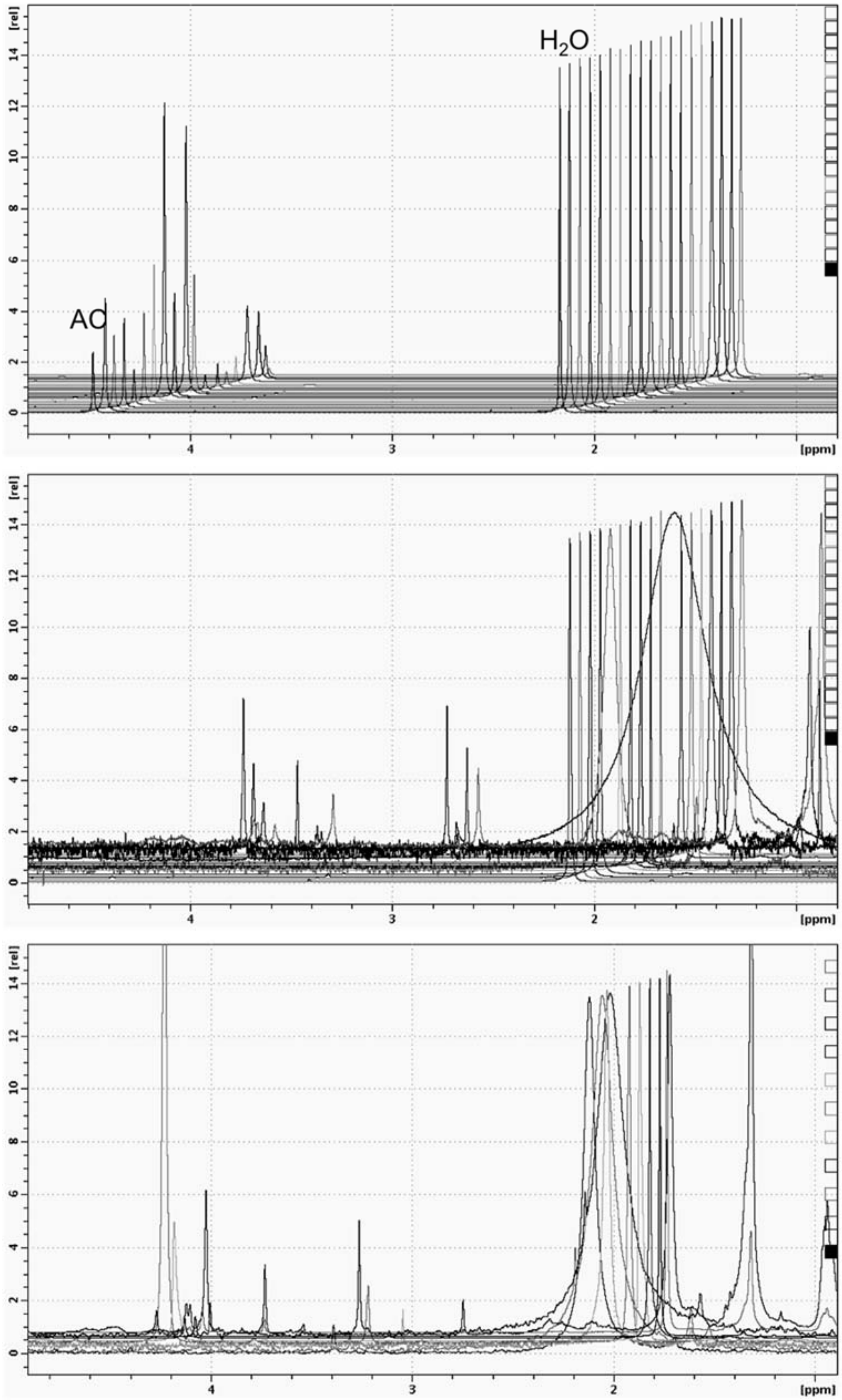

Figure 3. Stacked [1]H-NMR spectra of CK samples from each of the three vendors, with most recent spectra in the front. Spectra were normalized to the H_2O resonance at 2.17 ppm: (top) HP Gas, (middle) Semiconductor Resources, and (bottom) Custom Gas Solutions.

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ACRONYMS AND ABBREVIATIONS

AC	hydrogen cyanide
C_2Cl_4	ethylene tetrachloride
C_2N_2	cyanogen
CAS	chemical attribution signature
CCl_4	carbon tetrachloride
CG	phosgene
CK	cyanogen chloride
CO_2	carbon dioxide
ECBC	U.S. Army Edgewood Chemical Biological Center
FAC	Forensic Analytical Center
GC	gas chromatography
H_2O	water
NMR	nuclear magnetic resonance
PET	Protective Equipment Team
TCD	thermal conductivity detection

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APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	**CCl4**	**C2Cl4**	**AC**	**unk**	**Info from ^{1}H**	**N2/O2**	**CO2**	**NCCN**	**H2O**	**AC**	**CCl4**	**unk**
HP Gas, LLC	Aug-13	0.20				0.40	water & AC	0.05	1.51	1.57				0.02
HP Gas, LLC	Jun-13	0.80					water & AC	0.04	0.60	2.32			0.04	0.02
HP Gas, LLC	Jun-13	0.40					water & AC	0.01	1.32	1.28				
HP Gas, LLC	Jun-13	0.70		0.10			water & AC	0.02	1.05	2.02				0.02
HP Gas, LLC	Apr-13	0.10					water & AC	0.01	0.03	0.07			0.11	0.02
HP Gas, LLC	Oct-12	0.60		0.10			water & AC	0.02	0.34	1.55			0.36	
HP Gas, LLC	Oct-12	0.70	0.50	0.20			water & AC	0.02	2.39	2.04			0.45	
HP Gas, LLC	Oct-12	0.30	1.00	0.10			water & AC	0.01	0.46	1.37			0.22	
HP Gas, LLC	Sep-12	0.20	0.40	0.10			water & AC	0.02	0.80	0.72			0.46	
HP Gas, LLC	Sep-12	1.70					water & AC	0.01	0.28	2.49			0.01	
Custom Gas Solutions	Sep-12	0.50				0.30	broad water	0.02	0.08	1.01	0.01		0.11	
Custom Gas Solutions	Sep-12	No impurities seen by ^{13}C-NMR					broad water	0.02	0.06	0.31	0.01		0.13	
Custom Gas Solutions	Sep-12	0.80		0.20			broad water	0.02	2.70	2.56	0.01		0.06	
Custom Gas Solutions	Aug-12		0.30				broad water	0.01	0.02	0.08	0.00		0.29	
Semiconductor Resources	Feb-12	0.50					sharp water	0.70	0.30	0.80	0.30			
Semiconductor Resources	Feb-12	0.20					sharp water	0.80	1.20	1.20	0.20			
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.30	1.70	1.00	0.30			
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.10	0.10	0.70	0.20			
Semiconductor Resources	Nov-11	0.40	0.60	0.10			broad water	0.90	1.20	1.00	0.30			
Semiconductor Resources	Jun-11	No impurities seen by ^{13}C-NMR					sharp water	1.70	0.20	0.10	0.70			
Semiconductor Resources	Jun-11	0.30					sharp water, weak AC	1.90	0.05	0.50	0.70			
Semiconductor Resources	May-11	0.20					sharp water	2.10	0.02	0.60	0.40			
Semiconductor Resources	May-11	0.30					sharp water	2.00	0.02	0.20	0.40			
Semiconductor Resources	May-11	0.10					sharp water, weak AC	1.00	0.06	0.40	0.80	0.01		
HP Gas, LLC	Jan-11	0.50		trace			water & AC	0.80	0.04	0.50	0.20	0.07	0.10	
HP Gas, LLC	Jan-11	0.10					water & AC	0.80	0.04	0.30	0.30	0.03	0.05	
HP Gas, LLC	Jan-11	0.50		trace	trace		water & AC	1.20	0.09	1.10	0.50	0.10		
HP Gas, LLC	Jan-11	0.20		trace			water & AC	1.00	0.07	0.10	0.30	0.04	0.10	
HP Gas, LLC	Jan-11	0.40	0.30				water & AC	1.00	0.10	0.80	0.30	0.10	0.60	

APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	CCl4	C2Cl4	AC	unk	Info from ^{1}H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk
HP Gas, LLC	Dec-10	1.70	4.60	0.20	trace		water & AC	0.80	0.20	3.60	0.40	0.10	2.70	
HP Gas, LLC	Dec-10	0.80		0.20			water & AC	0.60	0.04	0.90	0.70	0.09		
HP Gas, LLC	Nov-10	1.20	0.70				water & AC	0.90	0.20	3.20	0.80	0.08	1.00	
HP Gas, LLC	Nov-10	1.00	2.10				water & AC	0.70	0.06	1.80	0.20	0.10	1.50	
Semiconductor Resources	Sep-10	1.10		trace			broad water	0.90	0.40	2.30	0.70			
HP Gas, LLC	Sep-10	0.70	1.20	0.20			water & AC	0.80	0.40	1.70	0.30	0.05	0.90	
Semiconductor Resources	Aug-10	1.80		0.20			sharp water	0.60			0.20			
Semiconductor Resources	Aug-10	0.80		0.10			sharp water	0.80	0.20	0.80	0.30			
Semiconductor Resources	Aug-10	1.10		0.10			sharp water			1.20		0.10	0.20	0.10
Custom Gas Solutions	Jul-10	No NMR data was collected for this sample								0.10			2.30	1.00
Custom Gas Solutions	Apr-10	1.10					water & AC	0.30	0.03	0.60	0.90	0.10	0.02	0.01
Custom Gas Solutions	Apr-10	0.60					water & AC	0.20	0.06	0.30	1.70	0.09	0.07	
Custom Gas Solutions	Apr-10		0.40				water & AC	0.40	0.01	0.01	1.20	0.04	2.60	0.02
Semiconductor Resources	Mar-10	0.20					many peaks	0.60	0.02	0.60	0.50			
Semiconductor Resources	Mar-10	0.20					strong water & AC	0.50	0.01	0.40	0.40			
Semiconductor Resources	Mar-10	0.40					many peaks	0.60	0.01	0.50	0.30			
Semiconductor Resources	Mar-10	0.40					weak water, strong AC	0.40	0.01	0.40	0.40			
Semiconductor Resources	Mar-10	1.10					weak water, many peaks	0.90	0.20	0.70	0.50			
Custom Gas Solutions	Feb-10	0.20		small			water & small AC	0.80	0.03	0.30	0.50	0.02	0.10	
Custom Gas Solutions	Jan-10	0.60	0.70				water & small AC	1.10	0.10	0.30	0.50		1.00	0.03
Custom Gas Solutions	Jan-10		1.20				AC & many other peaks	0.70	0.10	0.06	0.40		1.30	0.02
Custom Gas Solutions	Jan-10	No impurities seen by ^{13}C-NMR					water & others	0.90	0.06	0.30	0.30		0.20	0.02
HP Gas, LLC	Dec-09	2.60	3.80				water & AC	0.90	0.70	2.80	0.30	0.06	6.00	
HP Gas, LLC	Dec-09	2.20	3.30				water & AC	0.80	0.03	1.20	0.20	0.10	4.90	

APPENDIX A: Reverse Chronological Listing of Impurities Detected in Cyanogen Chloride Cylinders

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	**CCl4**	**C2Cl4**	**AC**	**unk**	**Info from ^{1}H**	**N2/O2**	**CO2**	**NCCN**	**H2O**	**AC**	**CCl4**	**unk**
HP Gas, LLC	Oct-09	No NMR data was collected for this sample						0.40	0.20	1.10	2.10	0.10	0.90	
HP Gas, LLC	Oct-09	No NMR data was collected for this sample						0.60	0.40	1.50	2.00	0.10	2.10	
Semiconductor Resources	May-09	No NMR data was collected for this sample						0.77	0.15	0.64	0.38		0.05	
Semiconductor Resources	May-09	No NMR data was collected for this sample						0.95	1.77	0.52	0.09		0.13	
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.36	0.00	0.64	0.30			
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.34		0.12	0.12		0.19	
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.80	0.02	0.46	0.18		0.11	
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.51	0.05	0.79	0.14		0.13	
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMR data was collected for this sample						N/A	N/A	2.60	0.03	0.26		
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMR data was collected for this sample						N/A	N/A		0.20	0.40		
Specialty Gases of America (Semiconductor Resources)	Oct-08			0.10	0.30		No ^{1}H data	N/A	N/A	0.17		0.40		
Stillwater (HP Gas, LLC)	Sep-08	0.40	3.10				water & AC	N/A	N/A	3.80		0.20	6.60	
Specialty Gases of America (Semiconductor Resources)	Mar-06	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	1.10				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	0.10				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	1.30				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	0.30				
TL2 Gases (HP Gas, LLC)	Mar-05	No NMR data was collected for this sample											5.20	
TL2 Gases (HP Gas, LLC)	Feb-05	No NMR data was collected for this sample											10.10	
TL2 Gases (HP Gas, LLC)	Jan-05	4.10					water & AC	No impurities were detected by GC/TCD						

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APPENDIX B: Listing of Impurities Detected in Cyanogen Chloride Cylinders from HP Gas, LLC

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	CCl4	C2Cl4	AC	unk	Info from ^{1}H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk
HP Gas, LLC	Aug-13	0.20				0.40	water & AC	0.05	1.51	1.57				0.02
HP Gas, LLC	Jun-13	0.80					water & AC	0.04	0.60	2.32			0.04	0.02
HP Gas, LLC	Jun-13	0.40					water & AC	0.01	1.32	1.28				
HP Gas, LLC	Jun-13	0.70		0.10			water & AC	0.02	1.05	2.02				0.02
HP Gas, LLC	Apr-13	0.10					water & AC	0.01	0.03	0.07			0.11	0.02
HP Gas, LLC	Oct-12	0.60		0.10			water & AC	0.02	0.34	1.55			0.36	
HP Gas, LLC	Oct-12	0.70	0.50	0.20			water & AC	0.02	2.39	2.04			0.45	
HP Gas, LLC	Oct-12	0.30	1.00	0.10			water & AC	0.01	0.46	1.37			0.22	
HP Gas, LLC	Sep-12	0.20	0.40	0.10			water & AC	0.02	0.80	0.72			0.46	
HP Gas, LLC	Sep-12	1.70					water & AC	0.01	0.28	2.49			0.01	
HP Gas, LLC	Jan-11	0.50		trace			water & AC	0.80	0.04	0.50	0.20	0.07	0.10	
HP Gas, LLC	Jan-11	0.10					water & AC	0.80	0.04	0.30	0.30	0.03	0.05	
HP Gas, LLC	Jan-11	0.50		trace	trace		water & AC	1.20	0.09	1.10	0.50	0.10		
HP Gas, LLC	Jan-11	0.20		trace			water & AC	1.00	0.07	0.10	0.30	0.04	0.10	
HP Gas, LLC	Jan-11	0.40	0.30				water & AC	1.00	0.10	0.80	0.30	0.10	0.60	
HP Gas, LLC	Dec-10	1.70	4.60	0.20	trace		water & AC	0.80	0.20	3.60	0.40	0.10	2.70	
HP Gas, LLC	Dec-10	0.80		0.20			water & AC	0.60	0.04	0.90	0.70	0.09		
HP Gas, LLC	Nov-10	1.20	0.70				water & AC	0.90	0.20	3.20	0.80	0.08	1.00	
HP Gas, LLC	Nov-10	1.00	2.10				water & AC	0.70	0.06	1.80	0.20	0.10	1.50	
HP Gas, LLC	Sep-10	0.70	1.20	0.20			water & AC	0.80	0.40	1.70	0.30	0.05	0.90	
HP Gas, LLC	Dec-09	2.60	3.80				water & AC	0.90	0.70	2.80	0.30	0.06	6.00	
HP Gas, LLC	Dec-09	2.20	3.30				water & AC	0.80	0.03	1.20	0.20	0.10	4.90	
HP Gas, LLC	Oct-09	No NMR data was collected for this sample						0.40	0.20	1.10	2.10	0.10	0.90	
HP Gas, LLC	Oct-09	No NMR data was collected for this sample						0.60	0.40	1.50	2.00	0.10	2.10	
Stillwater (HP Gas, LLC)	Sep-08	0.40	3.10				water & AC	N/A	N/A	3.80		0.20	6.60	
TL2 Gases (HP Gas, LLC)	Mar-05	No NMR data was collected for this sample											5.20	
TL2 Gases (HP Gas, LLC)	Feb-05	No NMR data was collected for this sample											10.10	
TL2 Gases (HP Gas, LLC)	Jan-05	4.10					water & AC	No impurities were detected by GC/TCD						

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APPENDIX C: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Semiconductor Resources

	Analysis	NMR data						GC/TCD data						
Manufacturer	date	NCCN	CCl4	C2Cl4	AC	unk	Info from ^{1}H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk
Semiconductor Resources	Feb-12	0.50					sharp water	0.70	0.30	0.80	0.30			
Semiconductor Resources	Feb-12	0.20					sharp water	0.80	1.20	1.20	0.20			
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.30	1.70	1.00	0.30			
Semiconductor Resources	Nov-11	0.30		0.10			sharp water	1.10	0.10	0.70	0.20			
Semiconductor Resources	Nov-11	0.40	0.60	0.10			broad water	0.90	1.20	1.00	0.30			
Semiconductor Resources	Jun-11	No impurities seen by ^{13}C-NMR					sharp water	1.70	0.20	0.10	0.70			
Semiconductor Resources	Jun-11	0.30					sharp water, weak AC	1.90	0.05	0.50	0.70			
Semiconductor Resources	May-11	0.20					sharp water	2.10	0.02	0.60	0.40			
Semiconductor Resources	May-11	0.30					sharp water	2.00	0.02	0.20	0.40			
Semiconductor Resources	May-11	0.10					sharp water, weak AC	1.00	0.06	0.40	0.80	0.01		
Semiconductor Resources	Sep-10	1.10		trace			broad water	0.90	0.40	2.30	0.70			
Semiconductor Resources	Aug-10	1.80		0.20			sharp water	0.60			0.20			
Semiconductor Resources	Aug-10	0.80		0.10			sharp water	0.80	0.20	0.80	0.30			
Semiconductor Resources	Aug-10	1.10		0.10			sharp water			1.20		0.10	0.20	0.10
Semiconductor Resources	Mar-10	0.20					many peaks	0.60	0.02	0.60	0.50			
Semiconductor Resources	Mar-10	0.20					strong water & AC	0.50	0.01	0.40	0.40			
Semiconductor Resources	Mar-10	0.40					many peaks	0.60	0.01	0.50	0.30			
Semiconductor Resources	Mar-10	0.40					weak water, strong AC	0.40	0.01	0.40	0.40			
Semiconductor Resources	Mar-10	1.10					weak water, many peaks	0.90	0.20	0.70	0.50			
Semiconductor Resources	May-09	No NMR data was collected for this sample						0.77	0.15	0.64	0.38		0.05	
Semiconductor Resources	May-09	No NMR data was collected for this sample						0.95	1.77	0.52	0.09		0.13	
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMR data was collected for this sample						N/A	N/A	2.60	0.03	0.26		
Specialty Gases of America (Semiconductor Resources)	Nov-08	No NMR data was collected for this sample						N/A	N/A		0.20	0.40		

APPENDIX C: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Semiconductor Resources

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	CCl4	C2Cl4	AC	unk	Info from ^{1}H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk
Specialty Gases of America (Semiconductor Resources)	Oct-08			0.10	0.30		No ^{1}H data	N/A	N/A	0.17		0.40		
Specialty Gases of America (Semiconductor Resources)	Mar-06	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	1.10				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	0.10				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	1.30				
Specialty Gases of America (Semiconductor Resources)	Oct-05	No impurities seen by ^{13}C-NMR					No ^{1}H data	N/A	N/A	0.30				

APPENDIX D: Listing of Impurities Detected in Cyanogen Chloride Cylinders from Custom Gas Solutions

Manufacturer	Analysis date	NMR data						GC/TCD data						
		NCCN	CCl4	C2Cl4	AC	unk	Info from ^{1}H	N2/O2	CO2	NCCN	H2O	AC	CCl4	unk
Custom Gas Solutions	Sep-12	0.50				0.30	broad water	0.02	0.08	1.01	0.01		0.11	
Custom Gas Solutions	Sep-12	No impurities seen by ^{13}C-NMR					broad water	0.02	0.06	0.31	0.01		0.13	
Custom Gas Solutions	Sep-12	0.80		0.20			broad water	0.02	2.70	2.56	0.01		0.06	
Custom Gas Solutions	Aug-12		0.30				broad water	0.01	0.02	0.08	0.00		0.29	
Custom Gas Solutions	Jul-10	No NMR data was collected for this sample								0.10			2.30	1.00
Custom Gas Solutions	Apr-10	1.10					water & AC	0.30	0.03	0.60	0.90	0.10	0.02	0.01
Custom Gas Solutions	Apr-10	0.60					water & AC	0.20	0.06	0.30	1.70	0.09	0.07	
Custom Gas Solutions	Apr-10		0.40				water & AC	0.40	0.01	0.01	1.20	0.04	2.60	0.02
Custom Gas Solutions	Feb-10	0.20		small			water & small AC	0.80	0.03	0.30	0.50	0.02	0.10	
Custom Gas Solutions	Jan-10	0.60	0.70				water & small AC	1.10	0.10	0.30	0.50		1.00	0.03
Custom Gas Solutions	Jan-10		1.20				AC & many other peaks	0.70	0.10	0.06	0.40		1.30	0.02
Custom Gas Solutions	Jan-10	No impurities seen by ^{13}C-NMR					water & others	0.90	0.06	0.30	0.30		0.20	0.02
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.36	0.00	0.64	0.30			
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.34		0.12	0.12		0.19	
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.80	0.02	0.46	0.18		0.11	
Custom Gas Solutions	Apr-09	No NMR data was collected for this sample						0.51	0.05	0.79	0.14		0.13	

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